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*Publication date:*  
2012

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### *Citation (APA):*

Binning, P. J., McKnight, U. S., Malaguerra, F., Rasmussen, J., Tuxen, N., Thorling, L., ... Bjerg, P. L. (2012). Pesticides in groundwater: modelling and data analysis of the past, present and future. Paper presented at 4th Joint Nordic Meeting on Remediation of Contaminated Sites, Oslo, Norway.

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# PESTICIDES IN GROUNDWATER: MODELLING AND DATA ANALYSIS OF THE PAST, PRESENT AND FUTURE

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## Abstract

Pesticides are the most frequently detected groundwater contaminants in Denmark. However, there is still a great deal of debate about the fate of pesticides and their future occurrence in our environment. We do not really understand the link between past usage and current observations, and are not well equipped to predict future trends in pesticide concentrations in groundwater. For example, we do not understand the difference between the loads from point and diffuse sources, or the impact of impurities and degradation products. We must also face the challenge that arises from the need to jointly manage our groundwater and surface water resources. Here, observed pesticide data is analyzed and combined with models to address these questions and needs. Groundwater and surface water pesticide observations reflect the fact that these two hydrological components have a strong interaction. For example, many older and banned pesticides are detected in streams and reflect the groundwater baseflow contribution to stream flow. Models of groundwater age and pesticide transport demonstrate the importance of geology and pumping regime in determining observed groundwater concentrations. Finally, management issues are addressed, eg. it is shown that it is important for pesticide management to consider both pumping strategies and manage surface application.

## Introduction

Pesticides are one of the most common causes for the closure of public water supply wells in Denmark [*Depotrådet*, 2011], and in 2009 they were detected in 37% of the wells sampled, with 12% being above water quality guidelines [*Thorling et al.*, 2010]. Up until the present time, the primary focus in Denmark has been on the impact of groundwater pesticides on groundwater based drinking water resources. However, with the EU Water Framework Directive, authorities are now being required to consider groundwater and surface water as a single entity.

This paper aims to present an overview of the pesticide problem in Denmark, with data and models being used to analyze the past, present and future occurrence of pesticides in our water resources. The past use of pesticides is reviewed, observation data on their current occurrence in surface and groundwater is presented, including a review of the impact of groundwater pesticides on surface water bodies. Models are used to explain trends in groundwater pesticide data and to speculate on the future fate of pesticides in the environment. Finally, models are used to show that the occurrence of pesticides in drinking water supplies depends not only on the application history of the pesticide in the water catchment, but also on the pumping strategy used at water supply wells. This suggests that well head management can assist in reducing the impact of pesticides on water supply.

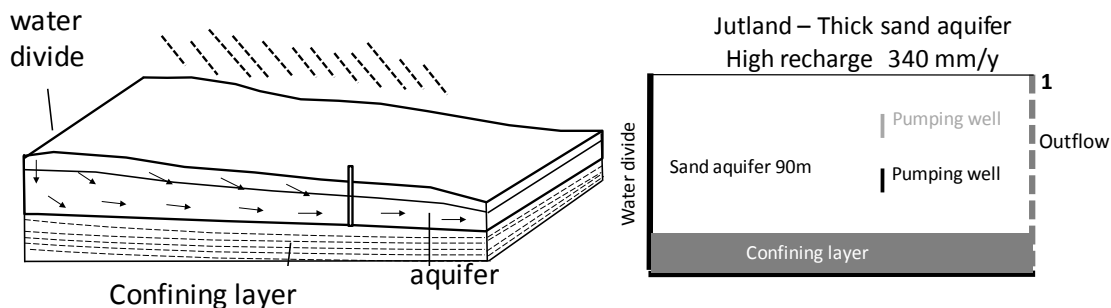
## Material and Methods

Two data sources are presented and conceptual and numerical models are used to analyze the current and future trends in pesticide data. The first data source is the Danish National database on the occurrence of pesticides in groundwater maintained by the Geological Survey of Denmark and Greenland (GEUS). The data includes monitoring results from approximately 3000 active water supply wells on Zealand and Jutland [Malaguerra *et al.*, 2012].

The second data source includes monitoring data collected by the authors in the catchment of the Hove and Nybølle streams on Zealand, Denmark. The study catchment has an area of 195 km<sup>2</sup> and is located west of Copenhagen. Approximately 80 % of the total catchment is used for agriculture; the rest is comprised of ca. 15 % natural area (i.e. forest and wetlands), and 5 % urban area (i.e. settlements and industry). There is significant groundwater abstraction for water supply at the junction of the Hove and Nybølle streams. Data collected includes pesticide concentrations in groundwater and surface water. The groundwater data is from both general monitoring wells [Malaguerra *et al.*, 2012] and from point sources such as contaminated sites in the catchment [Milosevic *et al.*, 2012].

Conceptual and numerical models are used to analyze the monitoring results and help understand pesticide fate. A number of conceptual models of groundwater/surface water systems are constructed with geologies typical for Danish environments (see figure 1). Groundwater age is simulated and coupled with information on pesticide application history and the results used to speculate on future trends. Direct simulations of pesticide transport from both diffuse and point sources are used to assist in the interpretation of monitoring results. All models are constructed using the software COMSOL Multiphysics.

**Figure 1.** Example of a conceptual model for simulating pesticide fate and transport processes

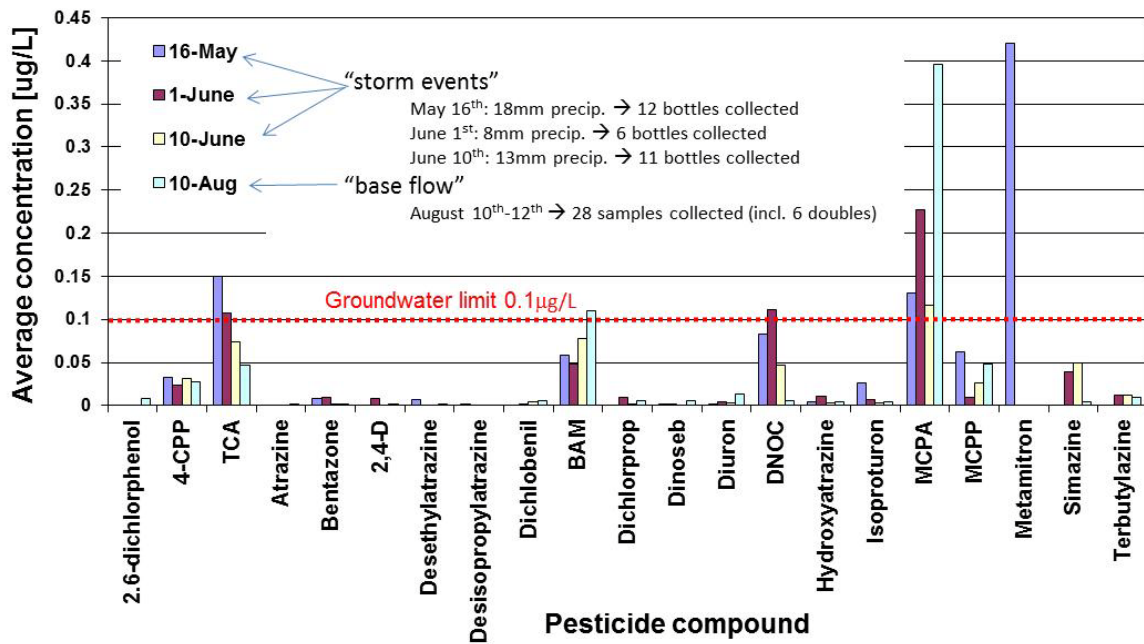


## Results

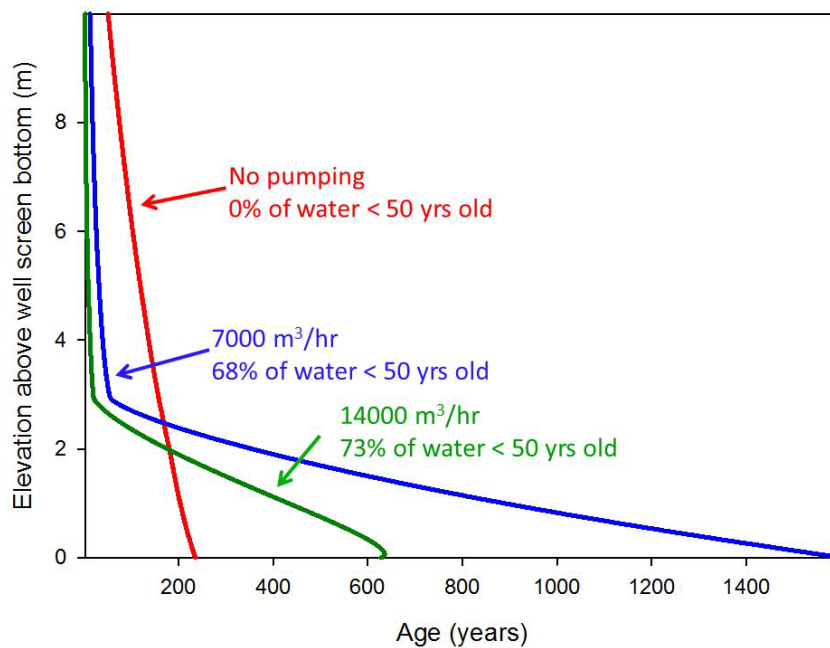
Examples of results are shown in figures 2 and 3. Figure 2 shows the observed surface water concentrations of pesticides on four sampling dates in 2010. Three of the sampling dates captured stormflows, while the fourth sampling date captured baseflow conditions.

Figure 3 shows example output from the models. The figure presents the age of water that can be expected in the pumping well shown in figure 1. The age varies with depth, with the oldest water being captured at the bottom of the well screen. It can be seen that the age distribution at the well screen depends on the pump rate, with higher pumping rates increasing the average age of water captured by the well, and also leading to the capture of younger water at the top of the well screen. These results can be coupled with pesticide application history to predict pesticide concentrations at drinking water wells.

**Figure 2.** Results from surface water monitoring in 2010 in the Hove/Nybølle catchment.



**Figure 3.** Results of a model of groundwater age, showing the age of water pumped at a well.



## Discussion and Conclusions

- Historical pesticide application will continue to affect groundwater for many decades in future [Chambon *et al.*, 2011].
- Observations of pesticides in groundwater and surface water reflect the strong interaction between these two hydrologic systems.

- Pesticides are found in groundwater more often near streams suggesting that groundwater/surface water flow processes affect the distribution of pesticides [Malaguerra *et al.*, 2012].
- The pesticide distribution is affected by geology. Observation data suggests that while clay layers do protect deeper groundwater, geochemistry also plays a role: aerobically degraded pesticides are less commonly found in unconfined sand aquifers because these are typically aerobic systems [Malaguerra *et al.*, 2012].
- Pesticides can be divided into several groups: i) old pesticides or degradation products, now banned, such as TCA, Dichloroprop or BAM, ii) old pesticides, still in use, such as MCPA, iii) new pesticides, currently in use, such as Metamitron, and iv) pesticides never permitted in Denmark. Monitoring results show that old pesticides are present at a constant level in streams. Since these pesticides are now banned, the pesticides must come from groundwater baseflow. In contrast, newer pesticides are primarily found in storm water flows in streams soon after their application on fields in the catchment. This suggests that they are not linked to groundwater flow. Finally, all groups of pesticides can be found in sediment, including some never permitted in Denmark such as lindane and chlorpyrifos.
- For many pesticides, observed surface water and groundwater concentrations do not reflect current usage. Rather they reflect the full historical usage patterns in the catchment.
- Analysis of observed pesticide concentrations in streams suggest that the most toxic pesticides are found in stream suspended sediment. The observed concentrations are high enough to lead to an ecological impact, even using recommended safety factors to account for decreased bioavailability [McKnight *et al.*, 2012].
- Pumping substantially increases the range of groundwater age captured by a drinking water well and increases the age of water captured in a well. The effect of pumping is not constant, and considerable variation in observed pesticide concentrations should be expected. Geology also affects pumped concentrations of pesticides, with models showing that the effect of pumping is strongly dependent on the geologic setting.
- While the current regulatory focus on source control is important for managing contamination to wells, it is important to consider the design of pumping strategies in order to control the transport of pesticides to the water wells and monitoring strategies for effective early warning and prediction.

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